CONF-9610205--5

ANL/TD/CP--91548

**ALUMINUM- U_3Si_2 INTERDIFFUSION AND ITS IMPLICATIONS FOR THE
PERFORMANCE OF HIGHLY LOADED FUEL OPERATING AT HIGHER
TEMPERATURES AND FISSION RATES***

G. L. Hofman, J. Rest, J. L. Snelgrove, and T. Wiencek

Argonne National Laboratory
9700 S. Cass Avenue
Argonne, IL 60439-4841 USA

S. Koster van Groos

Cornell University

IVED

DEC 09 1996

OSTI

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

To be Presented at the
1996 International Meeting on
Reduced Enrichment for Research and Test Reactors

October 7-10, 1996
Seoul, Korea

The submitted manuscript has been authored
by a contractor of the U. S. Government
under contract No. W-31-109-ENG-38.
Accordingly, the U. S. Government retains a
nonexclusive, royalty-free license to publish
or reproduce the published form of this
contribution, or allow others to do so, for
U. S. Government purposes.

*Work supported by the U.S. Department of Energy
Office of Nonproliferation and National Security
under Contract No. W-31-109-38-ENG

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

ALUMINUM- U_3Si_2 INTERDIFFUSION AND ITS IMPLICATIONS FOR THE PERFORMANCE OF HIGHLY LOADED FUEL OPERATING AT HIGHER TEMPERATURES AND FISSION RATES

G. L. Hofman, J. Rest, J. L. Snelgrove, and T. Wiencek

Argonne National Laboratory
9700 S. Cass Avenue
Argonne, IL 60439-4841 USA

S. Koster van Groos

Cornell University

ABSTRACT

Recent irradiation tests of U_3Si -Al dispersion fuel have shown performance limitations of this fuel when high volume fractions of U_3Si_2 operate at high temperatures and high fission rates. This potential problem is associated with high rates of Al- U_3Si_2 interdiffusion that may lead to complete consumption of matrix aluminum and the formation of excessive porosity.

INTRODUCTION

Aluminum- U_3Si_2 interdiffusion manifests itself by the formation of a single intermetallic compound, $U(AlSi)_3$, in the diffusion zone at the U_3Si_2 -Al interface -- the solubility of Al in U_3Si_2 itself being very small ($\ll 1$ at. %). $U(AlSi)_3$ has a composition intermediate between UAl_3 and USi_3 -- two cubic compounds that are mutually soluble. The Al-to-Si ratio is approximately 3.5 and the composition of the compound lies on the tieline between U_3Si_2 and Al, as shown in the isothermal section of the ternary equilibrium diagram^[1], (Fig. 1). The compound has a density of ~ 7.1 g cm⁻³ and approximately equal volumes of U_3Si_2 and Al are used in its formation. Consequently, there is only a small volume change, $\sim 4\%$, involved in the transformation of Al and U_3Si_2 to $U(AlSi)_3$.

Annealing experiments^{2,3,4]} with dispersion fuel samples have shown that the growth of the $U(AlSi)_3$ layer at the U_3Si_2 -Al interface obeys classical diffusion kinetics, i.e., the width of the width of the layer "Y" is described by: $Y = [K_0 \exp (-Q^h/RT)t]^{1/2}$ where Q^h is the activation energy for interdiffusion in $U(AlSi)_3$. K_0 is a reaction constant, t is time in seconds, T is the absolute temperature, and R is the gas constant.

Measurable layer formation occurs after several hundreds of hours at a temperature of around 400°C and at much shorter times at higher temperatures; however, at 300°C no interaction is observed after more than 1000 hours. Although the thermal diffusivity of aluminum in

$U(AlSi)_3$, per se is rather high, as has been found in similar compounds such as UAl_3 ^[5] and $ZrAl_3$ ^[6], it is still extremely low at aluminum-dispersion-fuel operating temperatures in current research reactors (normally well below 300°C).

Postirradiation examinations of U_3Si_2 -Al, however, do show a substantial and well-defined $U(AlSi)_3$ layer in fuel samples irradiated in ORR and HFIR at, respectively ~100°C and ~200°C, as shown in Fig. 2. It is a well-documented fact that at temperatures below approximately 1/2 the absolute melting temperature of a solid (in the case of $U(AlSi)_3$, this is 835 K or 562°C), diffusion can be enhanced by irradiation. The postirradiation microstructure of an U_3Si_2 -Al dispersion sample made with depleted U, shown in Fig. 1 and irradiated alongside similar LEU samples shows that the $U(AlSi)_3$ formation is clearly due to fission damage, since it is not measurably present in the DU sample.

Al- U_3Si_2 INTERDIFFUSION DURING IRRADIATION

Experimental Data

Postirradiation data from two U_3Si_2 -Al dispersion fuel irradiation test programs were used, from the RERTR miniplate program carried out in the Oak Ridge Research Reactor (ORR) and the ANS fuel development program performed in the High Flux Isotope Reactor (HFIR). The fuel temperature (i.e., the temperature of the dispersion or fuel meat, in all the ORR samples was normally ~100°C or less while the fission rate of the samples varied somewhat depending on irradiation position, but more so depending on the enrichment of the fuel used, i.e., LEU, MEU, or HEU. The bulk of the samples however consisted of LEU. The fuel temperatures in the HFIR tests spanned a range from 100°C to 425°C; the fission rate also varied with enrichment but was on the whole one-to-two orders of magnitude higher in this high flux reactor. The extent of interdiffusion was measured by optical metallography and scanning electron microscopy (SEM). Compositional information was obtained by SEM-EDX.

Examples of ORR and HFIR LEU samples are shown in Fig. 3. In both cases the interdiffusion zone at the fuel particle periphery is clearly distinguishable -- it is substantially wider in the HFIR sample that ran at a higher temperature and much higher fission rate. The data used in this study are collected in Table I.

Analysis

Enhanced diffusion during irradiation is the result of point defects (vacancies and interstitials) created in excess over the thermal equilibrium concentration by, in the case of fuel, fission fragments. The magnitude of the enhancement depends therefore on the damage rate -- fission rate in this case. The behavior of the point defects upon formation determines the functional relationship between fission rate and diffusivity. Annihilation of the created vacancies and interstitials by mutual recombination results in a square root fission rate dependence while a linear dependence prevails when annihilation occurs at sinks. The temperature dependence of radiation enhanced diffusivity varies from a-thermal for the latter case to an Arrhenius dependence for the former with an activation energy of one-half the migration energy for vacancies -- roughly one quarter of the activation for thermal diffusivity.

TABLE I DATA OF SAMPLES USED FOR U ₃ Si ₂ -Al INTERDIFFUSION CORRELATION						
Sample	Enrichment	U-235 Depletion, %	Temp., °C	t, 10 ⁶ s	Fission Rate, 10 ¹⁵ cm ³ s ⁻¹	Zone Width, 10 ⁻⁴ cm
ORR-100	LEU	45	100	15.1	0.13	2.0
ORR-92	LEU	85	100	21.9	0.21	4.0
ORR-93	LEU	93	100	34.7	0.14	4.4
ORR-34	LEU	90	100	25.9	0.18	3.4
ORR-123	MEU	44	100	11.0	0.38	2.2
ORR-124	MEU	69*	100	23.8	0.26	2.8
ORR-121	HEU	44*	100	11.2	0.84	3.2
ORR-122	HEU	69*	100	23.5	0.61	4.4
ORR-125	LEU	34	100	12.3	0.32	2.2
ORR-99	LEU	79	100	30.8	0.14	4.0
ORR-36	LEU	97	100	33.3	0.13	3.6
HFIR 3-1	HEU	74*	100	1.98	8.1	5.0
HFIR 3-14	HEU	88*	200	1.98	10.1	18.0
HFIR 3-10	LEU	91	200	1.98	2.5	10.0

*High total U burnup samples.

To define the process of U₃Si₂-Al interdiffusion in such fundamental terms would require very controlled experiments. The present analysis, instead, attempts to use the available postirradiation data to derive a useful correlation that is consistent with the physics of radiation damage.

The fission enhanced formation of the U(AlSi)₃ interdiffusion zone "Y" between U₃Si₂ and aluminum may be expressed by:

$$Y = \left[K(F)^n \exp - \left(\frac{Q}{RT} \right) \cdot (t - t_0) \right]^{1/2} \quad (1)$$

where k is a materials constant,

T is the dispersion temperature in K,

Q is the activation energy,

(t - t₀) the irradiation time minus an incubation time allowing for the establishment of a sound U₃Si₂-Al bond, and

F is the fission rate in the U_3Si_2 particles.

The best fit through the LEU and MEU data was obtained with the following parameters:

$$Q = 5870 \text{ cal/mole}$$

$$K = 1.1 \times 10^{-95}$$

$$n = 1$$

$$t_0 = 3.9 \times 10^{-6} \text{ s}$$

The linear fission rate dependence permits the data to be expressed in terms of

$$Y^2/\langle F \rangle \text{ vs } t$$

where $\langle F \rangle$ is the time average fission rate or, in effect, the final fission density FD divided by irradiation time. All the LEU and the low burnup MEU data fit the correlation rather well, as shown for the 100°C data in Fig. 4. A variation in irradiation temperature of 12°C , is a reasonable considering flux variations and microstructural changes during the long irradiation history of the samples. The temperature dependence (shown in Fig. 5) had to rely on only two temperatures and is therefore a bit tenuous; however both fission rate and temperature dependence are consistent with models of radiation enhanced diffusion and do represent the LEU data rather well.

It proved not possible to include the high burnup MEU and HEU samples in the correlation with any reasonable fission rate dependence. The reason for this can be found in the morphology of the interdiffusion zone. As shown in Fig. 6, the interdiffusion zone for the high burnup MEU sample contains globular features while the zone for the LEU sample has a very smooth appearance. It is reasoned that the features in the MEU sample impede the interdiffusion; indeed, a change in the pre-exponential factor K from 1.1 to 0.4×10^{-25} results in a good fit of all high burnup data, as shown in Fig. 7. Since the RERTR program is concerned with LEU, the different behavior of fuels that are burned well beyond full LEU burnup is at this point primarily of academic interest. For the purpose of evaluating LEU behavior over a wide range of operating temperatures and fission rate equation (1) can be combined with a separate thermal diffusion equation derived from out of reactor annealing tests on U_3Si_2 -Al dispersion fuel plates

$$Y^{th} = \left[K \exp - \left(\frac{Q}{RT} \right) \right]^{1/2} \quad (2)$$

The composite (sum) of these two equations is shown in Fig. 8. In addition to some of the data from Table I, a few data points from other experiments are included for comparison. Depending on the fission rate, thermal diffusion dominates from about 400°C upwards but the interdiffusion is controlled by fission at the lower temperatures that prevail in most research reactor applications.

DISCUSSION AND CONCLUSIONS

What, then, does this rate of interdiffusion mean in terms of U_3Si_2 -Al dispersion fuel behavior? Clearly at the low temperatures and moderate fission rates that exist in most research reactors the formation of thin interaction zones at the fuel particle surfaces has no discernable effect. However, as the latest HFIR tests have shown the effects can be dramatic at higher operating temperatures and fission rates. This is shown in Figs. 2 and 9 for nominally 4.8 gUcm^{-3} (43 vol. % U_3Si_2) LEU dispersion samples irradiated at temperatures currently estimated to be 200°C , 300°C and 400°C , respectively. In the 200°C sample the interdiffusion zone width is substantial but the overall fuel meat microstructure is essentially similar to that of the ORR samples. At 300°C , however, the interdiffusion process has virtually consumed all matrix aluminum and crack-like voids have developed at the erstwhile fuel particle surfaces. In the 400°C sample these voids have developed to occupy approximately 50% of the meat volume, clearly any fuel plate should have pillowed under these conditions. It appears that this phenomenon is associated with the disappearance (through interdiffusion) of the matrix aluminum. It is therefore sensitive to the amount of aluminum available i.e., the fuel loading as well as the interdiffusion rate. This is parametrically illustrated in Fig. 10 and Fig. 11 where the calculated change in aluminum matrix volume is plotted versus fission density. No fission rate effects appear in these calculations because, as mentioned earlier, the diffusivity depends linearly on the fission rate which allows the product of time and fission rate, i.e., fission density, to be used as a parameter.

As the curves in Figs. 10 and 11 show it is the combination of high loading and temperature that lead to conditions where matrix aluminum may be consumed at realistic maximum burnup levels. With the present data it is not possible to state whether complete aluminum consumption alone is a sufficient condition to trigger excessive void formation or whether a second condition, high fission rate, is also required. A test at high temperature but low fission rate may resolve this question. Since excessive void formation has never been observed prior to aluminum depletion, even at the high fission rates in the HFIR test, we are confident that this phenomenon can be avoided by placing appropriate limits on burnup (fission density).

REFERENCES

1. A. E. Dwight, "A Study of the Uranium-Aluminum-Silicon System," Argonne National Laboratory Report ANL-82-14 (September 1982).
2. S. Nazaré, "Low Enrichment Dispersion Fuels for Research and Test Reactors," J. Nucl. Mater. 124, 14-24 (1984).
3. T. C. Wiencek, R. F. Domagala, and H. R. Thresh, "Thermal Compatibility Studies of Unirradiated Uranium Silicide Dispersed in Aluminum," Nucl. Tech. 71, 608-616 (1985).
4. G. L. Garner, K. E. Bogacik, and J. W. Oswood, "LEU Silicide Programs at Babcock and Wilcos," Proc. 1986 Int. Mtg. on Reduced Enrichment for Research and Test Reactors, Galtlinburg, Tennessee, November 2-6, 1986, Argonne National Laboratory Report ANL/RERTR/TM-9, CONF-861185, pp. 80-115 (May 1988).

5. L. S. Castleman, "Layer Growth During Interdiffusion in the Aluminum Uranium Alloy System," J. Nucl. Mater., 3, 1, 1-15 (1961).
6. G. V. Kidson and G. D. Miller, "A Study of the Interdiffusion of Aluminum and Zirconium," J. Nucl Mater. 1, 12, 61-69 (1964).
7. M. Ugajin, M. Akabori, A. Itoh, H. Someya, T. Nakagana, and K. Ohsawa, "Capsule Irradiation Tests of U-Si and U-Me (Me = Fe, Ni, Mn) Alloys for Use in Research Reactors," Proc. 16th Int. Mtg. on Reduced Enrichment for Research and Test Reactors, Oarai, Japan, October 4-7, 1993, Japan Atomic Energy Research Institute Report JAERI-M 94-042, pp. 175 - 182 (March 1994).
8. E. Groos, H.-J. Bückner, H. Derz, and R. Schröder, "Nachbestrahlungsuntersuchungen an Testplatten für niedrig angereicherte Brennelemente für Forschungsreaktoren," Kernforschungsanlage Jülich GmbH Report Jül-Spez-469 (July 1988).

PARTIAL TERNARY DIAGRAM

Fig. 1. Isothermal Section of U-Si-Al equilibrium diagram showing solubility ranges of ternary compounds.

Plate A34, ORR, 300 days at -100°C
 3.7 g cm^{-3} LEU, $\sim 90\%$ Bu

(500x)

HANS-3-10, HFIR, 24 days at 200°C
 4.6 g cm^{-3} LEU, 90% Bu

(500x)

Fig. 2. $\text{U}(\text{AlSi})_2$ interaction layer (light grey) in $\text{U}(\text{Si})_2\text{-Al}$ dispersion fuel irradiated in ORR and HFIR

Fig. 3. U-Si-Al dispersion with DU irradiated in ORR for 250 days, showing no $\text{U}(\text{AlSi})_2$ layer.

Fig. 4. Interdiffusion Correlation and Measured Interaction Widths for LEU Samples Irradiated in ORR at $\sim 100^\circ\text{C}$

Fig. 5. Calculated and Measured Interaction Widths for LEU Samples Irradiated in ORR and HFIR at 100 and 200°C

Fig. 6 Comparison of interaction Zone Structure
upper: LEU (70% Bu), lower: HEU (70% Bu)

Fig. 7. Correlation and Measured Interaction Widths for High Uranium Burnup (MEU and HEU) Samples Irradiated in ORR and HFIR at 100°C

Fig. 8. Rate of $\text{U}(\text{AlSi})_3$ layer formation as a function of temperature and fission rate.

HANS 3-18, 24 days at -300 C, LEU, -75% Bu

(250x)

HANS 3-17, 24 days at -400 C, LEU, -75% Bu

(250x)

Fig. 3 Meat microstructure of 4.6 g cm^{-3} U/Si, LEU fuel irradiated in HIFR at high burnup and high temperature.

Fig. 10.

Diminution of aluminum in the fuel meat as a function of fission density in the fuel particles for various fuel loadings for $T = 200^\circ\text{C}$.

Fig. 11 Diminution of aluminum in the fuel meat as a function of fission density in the fuel particles for various fuel meat temperatures for $\text{pu} = 4.8 \text{ g cm}^{-3}$.